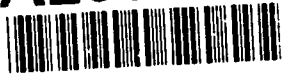


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13. ABSTRACT (Maximum 200 words) Research on chemical vapor deposition (CVD) of diamond films is summarized. The development of a technique for High Sensitivity Absorption Spectroscopy at deep ultraviolet wavelengths in CVD systems is reported. Diagnostic experiments on the diamond CVD environment are described.					
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Final Report on
A High Flux Radical Beam for Diamond Growth

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Period of Grant: April 30, 1990 to April 29, 1993

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Authors: J. E. Lawler and L. W. Anderson

Summary of Principle Findings

The goal of this investigation was to understand the microscopic physics and chemistry of diamond film growth. Our original research plan was to grow diamond films under conditions such that the flux of atoms and molecules to the surface is both known and highly controlled. A molecular beam system capable of producing a high flux of chemical radicals was developed and used in many attempts to grow diamond films under molecular beam conditions. Many fundamental experiments on the physics and chemistry of diamond film growth would be possible under molecular beam growth conditions. Although we succeeded in growing hard carbon films with the molecular beam system, the diamond content of the film was low. We now suspect that higher order surface chemistry is very important in diamond film growth. The steady state coverage of the growth surface with chemical radicals is proportional to the incident flux density of the radicals. The attainable radical flux density in a molecular beam is much lower than in a conventional 20 Torr diamond chemical vapor deposition (CVD) system. Higher order surface chemistry is greatly inhibited by the resulting lower steady state coverage of the growth surface with molecular radicals.

Our research plan was subsequently modified to emphasize advance spectroscopic diagnostics which are applicable to a typical 20 Torr diamond CVD system. Our primary goal of understanding the microscopic physics and chemistry of diamond growth was unchanged. We developed and used a powerful new technique for high sensitivity white light absorption spectroscopy in the ultraviolet (UV) and vacuum ultraviolet (VUV).¹ This technique has been used to study the production, transport, and destruction of key gas phase radicals in the CVD of diamond such as the methyl radical (CH_3), acetylene (C_2H_2), and CH .

The high sensitivity absorption experiment uses an ultra-stable Xe arc lamp as a source of continuum radiation for absorption measurements in the deep ultraviolet (216 nm for CH_3 and 195 nm for C_2H_2). The radiation from the arc lamp, after transmission through the diamond growth environment, is sent into a spectrometer equipped with a photodiode array.

This simple experiment, because of the good stability of the arc lamp and multi-element detector array, is extraordinarily sensitive, being able to detect fractional absorptions as small as 5×10^{-5} or less. The detector array is essential because it makes the experiment insensitive to slow drifts in the arc lamp radiation. A single element, sequentially scanned experiment is very sensitive to arc lamp drift. The detector array also has an advantage in that it simultaneously accumulates good photon statistics in all spectral elements across the absorption feature. This second advantage is important once the absorption experiment becomes limited by Poisson (photon) statistics. This experiment now has a detection limit of about $2 \times 10^{11} \text{ cm}^{-3}$ for CH_3 . This experiment is already better than all competing spectroscopic techniques for detecting CH_3 because of its sensitivity and linearity. Competing spectroscopic techniques for detecting CH_3 include infrared diode laser absorption spectroscopy which suffers from low sensitivity, resonance enhanced multiphoton ionization which is difficult to calibrate absolutely because of its nonlinearity, and coherent antistokes Raman spectroscopy which has low sensitivity and is also nonlinear and difficult to calibrate absolutely. The CH_3 radical has no excited electronic states which are stable against dissociation, thus laser induced fluorescence cannot be used to detect CH_3 . The development of a simple, highly sensitive technique for absolute density measurements on CH_3 is a major breakthrough. This experimental technique has been used in hot filament growth systems and in glow discharge growth systems.^{1,2,3} and will be useful for many other systems. A digital subtraction technique is being used to discriminate against line emission from the glow discharge and detect only the continuum emission from the arc discharge. The continuum emission from the arc discharge has absorption features after traversing the glow discharge.

After demonstrating the technique for high sensitivity absorption spectroscopy in both hot filament and glow discharge diamond CVD systems,^{1,2} we used it to measure the effective activation energy for CH_3 production from both methane (CH_4) and tert butyl peroxide ($(\text{CH}_3)_3 \text{COOC} (\text{CH}_3)_3$).³ We also used the high sensitivity absorption experiment to study the rapid isotopic exchange of hydrogen (H) atoms and deuterium (D) atoms in the methyl radical under typical diamond growth conditions.⁴ These isotopic exchange reactions are important for two reasons: (1) the interpretation of isotopic labeling experiments which have and are being used to study diamond growth is greatly affected by rapid "scrambling" of isotopic mixtures in the gas phase, and (2) one of the most attractive schemes we have devised for measuring the absolute H density involves absorption spectroscopy on the Lyman-alpha transition of D. The use of a rare isotope is necessary because the Lyman-alpha transition of H produces such deep absorption signals that they are difficult to quantify.

Our most substantive study, thus far, using high sensitivity absorption spectroscopy has recently been submitted for publication.⁵ In this investigation we measured: the CH_3

density, the C_2H_2 mole fraction, the hot filament properties, the diamond growth rate, and diamond film quality as a function of time, filament temperature, and feed gas mixture in a hot filament diamond CVD system. The effects of filament surface poisoning and bulk carburization were studied in a highly quantitative fashion. We also saw evidence that many of the important reactions which produce and destroy CH_3 are in partial equilibrium under typical diamond growth conditions. For example, the CH_3 density was found to be determined primarily by the net carbon content of the feed gas, and thus was quite similar for 2% CH_4 and for 1% C_2H_2 in the feed gas.

Other spectroscopic studies have been performed as part of this project. The potential of laser photoacoustic spectroscopy for measuring concentrations of molecular radicals in typical diamond CVD systems has been investigated. We identified molecular bands which can be observed in emission from a glow discharge diamond CVD system, and which can be used to derive a reliable gas kinetic temperature from the rotational temperature of the band.⁶ We also studied the temperature dependence of diamond film morphology.⁷

Our continuing research on the physics and chemistry of diamond CVD will likely emphasize high sensitivity absorption spectroscopy. This technique has the potential to provide accurate spatial maps of the absolute density of all the key gas phase species in the diamond growth environment. Such maps, when combined with a modeling effort, will produce a much more detailed understanding of the microscopic physics and chemistry of diamond growth.

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